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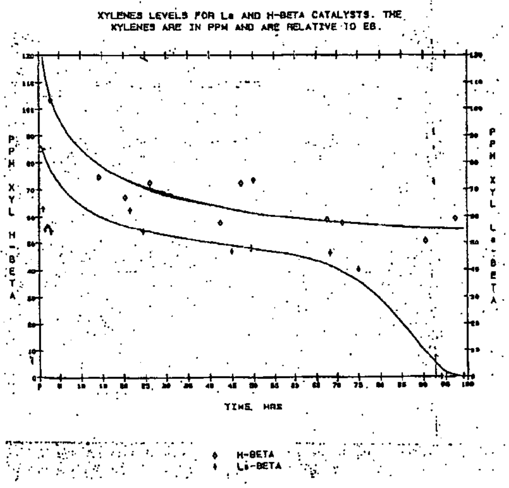
(54) Modified zeolite alkylation catalyst and process employing same.

(57) A metal modified alkylation catalyst comprising a lanthanum/beta zeolite is provided, The lanthanum/beta zeolite has a surface area based upon the crystalline structure of the lanthanum/beta zeolite of at least 600m^2/g and a sodium content in the crystalline structure of the lanthanum/beta zeolite of less than 0,04 weight percent Na$_2$O.

A process for the preparation and utilization of the lanthanum/beta zeolite is also provided. The process is particularly useful for the alkylation of an aromatic substrate in the liquid phase by a low molecular weight alkylating agent. A specific process involves the alkylation of benzene with ethylene to produce ethylbenzene. The process is carried out in the liquid phase and at alkylation condition under which the xylene make, based upon the amount of ethylbenzene produced, is no more than 0.03 weight percent.

Figure 1



EP 0 507 761 A1

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TECHNICAL FIELD OF THE INVENTION

This invention relates to an improved, metal-modified, alkylation catalyst and the process for employing such catalyst. The catalyst comprises a lanthanum/beta zeolite which is particularly useful in the alkylation of an aromatic substrate in the liquid phase by a low molecular weight alkylating agent.

BACKGROUND OF THE INVENTION

Processes fon the alkylation of aromatic feedstocks and the use of molecular sieves as catalysts in such alkylation processes are well known in the art. Such alkylation processes may be used to produce mono-/or poly-alkylated products ranging from low to high molecular weights and may be carried out in the vapor phase, in the liquid phase, or under intermediate conditions in which both liquid and vapor phases exist.

U.S. Patent No. 4,301,116 to Young discloses the use of a crystalline zeolite alkylation catalyst in the alkylation of benzene by relatively long chain length alkylating agents having one or more reactive alkyl groups of at least five carbon atoms. The reactants may be in either the vapor phase or the liquid phase, and the zeolite catalyst may be either modified or unmodified. Preferred zeolite catalyst include zeolite beta, ZSM-4, ZSM-20, ZSM-38, and synthetic and naturally occurring isotopes thereof, such as zeolite omega and others. The zeolites may be subjected to various chemical treatments, and may also be subjected to thermal treatments, including steam or calcination in air, hydrogen or an inert gas. Specifically disclosed in Young is the reaction of benzene and 1-dodecene over zeolite beta in a flow reactor at 250°c and 600psig.

U.S. Patent No. 4,185,040 to Ward et al. discloses an alkylation process employing a molecular sieve catalyst of low sodium content which is said to be especially useful in the production of ethyl benzene from benzene and ethylene, and cumene from benzene and propylene. The Na_2O content of the zeolite should be less than 0.7 weight percent and preferably less than 0.5 weight percent. examples of suitable zeolites include molecular sieves of the X, Y, L, B, ZSM-5, and Omega crystal types, with steam stabilized hydrogen Y zeolite being preferred. The alkylation process is preferably carried out under conditions in which at least some liquid phase is present, at least until substantially all of the olefin alkylating agent is consumed.

Another alkylation procedure is disclosed in U.S. Patent Nos. 4,798,816 and 4,876,408 to Ratcliffe et al. Ratcliffe et al. employ molecular sieve alkylation catalyst which have been treated in a manner to improve selectivity to monoalkylation, specifically to the propylation of benzene to produce cumene. selectivity is said to be increased by at least one percentage point by first depositing a carbonaceous material on the catalyst and then subjecting the resultant carbon containing catalyst particles to combustion. Specifically disclosed zeolitic crystalline molecular sieves include those selected from the group of Y zeolites, fluorided Y zeolites, X zeolites, zeolite beta, zeolite L and zeolite omega. The zeolites may be modified to arrive at products of reduced alumina content and reduced sodium content.

Aromatic alkylation reactions such as the alkylation of benzene with ethylene are highly exothermic reactions. As a result the alkylation reactions may be carried out in stages with intermediate cooling steps. For example, U.S. Patent No. 4,107,224 to Dwyer discloses the vapor phase ethylation of benzene over a zeolite catalyst in a down flow reactor with the intermediate injection of cold reactants in a diluent. Specifically disclosed is the interstage injection of ethylene and benzene. Dwyer characterizes the catalyst suitable for use in his invention in terms of those having a constraint index within the approximate range of one to twelve. Suitable zeolites, with the constraint index in parenthesis, are ZSM-5 (8.3), ZSM-11 (8.7), ZSM-12 (2), ZSM-35 (4.5), ZSM-38 (2) and similar materiale. Various molecular sieves including, inter alia, zeolite beta (constraint index 0.6), are disclosed as having constraint indices outside of the range suitable for the Dwyer ethylbenzene production process.

U.S. Patent No. 4,891,458 to Innes is directed to a process for the alkylation or transalkylation of an aromatic hydrocarbon with a C_2 to C_4 olefin alkylating agent under at least partial liquid phase conditions utilizing zeolite beta as the catalyst.

SUMMARY OF THE INVENTION

In accordance with the present invention there is now provided a metal-modified alkylation catalyst and process for employing such catalyst in the alkylation of aromatic substrates with relatively low molecular weight alkylating agents. Although it is preferred that the catalyst be utilized under moderate temperature conditions, including liquid-phase conditions, the catalyst may also be utilized in vapor phase operation. The catalyst comprises a metal-modified zeolite beta, preferably a lanthanum/beta zeolite which is characterized by having a lanthanum content of between about 0.05 and 0.5 weight percent, and preferably about 0.1 weight percent. Although it is preferred that the beta zeolite be modified with lanthanum, other metals such as calcium and barium may also utilized.

The lanthanum/beta catalyst of the present invention can be prepared by first subjecting a parent zeolite beta to ammonium exchange, calcining the resultant dried powder to burn the organic template, subjecting the calcined powder to additional ammonium exchange, and then incorporating lanthanum into the zeolite system by ion-exchange method. A binder is then added and the mixture pelletized by any suitable means. Subsequent calcination then places the catalyst in its active LaH-Beta form.

In carrying out the process of the present invention, a feedstock containing an aromatic substrate is supplied to a reaction zone and brought into contact with the molecular sieve alkylation catalyst comprising lanthanum/beta zeolite. The lanthanum/beta zeolite preferably has a lanthanum content of approximately 0.1 weight percent and is further characterized by a surface area of at least 500 m^2/gram, more preferably at least 650m^2/gram, based upon the crystalline zeolite beta. A C_2 to C_4 alkylating agent is also supplied to the reaction zone which is preferably operated under temperature and pressure conditions to maintain the aromatic substrate in the liquid phase, while causing alkylation of the aromatic substrate in the presence of the alkylation catalyst. The resulting alkylated aromatic substrate is then recovered from the reaction zone.

A preferred application of the present invention is In the alkylation of benzene with ethylene to produce ethylbenzene. The process is carried out in liquid phase, as noted above, and at alkylation conditions under which the xylene make, based upon the amount of ethylbenzene produced, is no more than 0.03 weight percent. In another embodiment of the invention, liquid-phase alkylation is carried out using a plurality of series connected reaction stages operated at an average temperature of no more than 300°C with the interstage injection of the C_2 to C_4 alkylating agent in a manner to maintain at least one mole percent of alkylating agent solubilized in the aromatic substrate. A schematic showing the preferred embodiment for carrying out the present alkylation process by employing a plurality of series connected reaction stages is shown in copending application Serial No. 371,500, the entire disclosure of which is incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a graph showing the results of experimental work of the alkylation of benzene with ethylene over the catalyst of the present invention as compared to an unmodified zeolite beta.

DETAILED DESCRIPTION

The present invention relates to an improved alkylation catalyst and the process for employing such catalyst. the preferred catalyst comprises a lanthanum/beta zeolite which is particularly useful in the alkylation of an aromatic substrate by a low molecular weight alkylating agent. The invention is especially applicable to the ethylation of benzene under mild liquid-phase conditions producing little or no xylene make, and the invention will be described specifically by reference to the production of ethylbenzene. However, other alkylating reactions may be utilized in carrying out the invention. For example, the invention may be applied to the reaction of propylene with benzene to produce cumene. Also, while olefinic alkylating agents normally will be employed, other alkylating agents such as alkynes, alkyl halides, alcohols, ethers, and esters as disclosed, for example in U.S. Patent 3,551,510 to Pollitzer et al. may be used. Other aromatic substrates such as toluene and xylene may also be subject to alkylation in accordance with the invention. Further, while the present invention is particularly useful for liquid-phase operations, vapor phase or mixed liquid/vapor phases may also be employed.

It has been previously shown that zeolite beta in its H-form is a very good catalyst for liquid-phase alkylation. The preferred lanthanum/beta catalyst of the present invention, however, exhibits better selectivity to xylene formation than does its hydrogen counterpart.

The lanthanum/beta zeolite of the present invention can be prepared by modification of the crystalline zeolite beta. Basic procedures for the preparation of crystalline zeolite beta which is identified by its x-ray defraction pattern are disclosed in U.S. Patent 3,308,069 to Wadlinger et al. Additionly, European Patent Application 159,846 to Reuben discloses the synthesis of zeolite beta having a silica/alumina mole ratio of up to 300 by employing a templating agent formed by the combination of dimethyl benzyl amine and benzyl halide. Other methods for the preparation of zeolite beta are disclosed in European Patent Application 165,208 to Bruce et al., European Patent Application 186,447 to Kennedy et al., and U.S. Patent No. 4,642,226 to Calvert et al. Each of these procedures is known in the art and suitable for preparing the crystalline zeolite beta useful in the present invention, and the entire disclosures of the above-referenced patents are incorporated herein by reference.

The parent zeolite beta catalyst employed in the present invention most preferably is of ultra-low sodium content. Although low sodium content zeolite betas are, in themselves, known in the art (U.S. Patent Nos. 3,308,069 to Wadlinger et al. and 4,642,226 to Calvert et al.) the preferred parent zeolite beta employed in the present invention is characterized by a sodium content substantially lower than those disclosed in the Wadlinger et al. and Calvert et al. patents. Preferably, the parent zeolite beta utilized in the present invention has a sodium content of less than 0.04 weight percent, and most preferably less than 0.02 weight percent, expressed as Na_2O. Such preferred parent zeolite beta is also characterized in terms of a very high surface area, specifically at least $600 m^2/g$ based upon the crystalline zeolite beta.

The preferred parent zeolite beta is produced by means of a series of ion-exchange and calcination procedures carried out employing as synthesized zeolite beta as a starting material. The synthesized zeolite beta can be produced by hydrothermal digestion of a reaction mixture comprising silica, aluminia, sodium or other alkyl metal oxide, and an organic templating agent in accordance with any suitable procedure such as those disclosed in the aforementioned U.S. patents to Wadlinger et al. and Calvert et al.

Typical digestion conditions include temperatures ranging from slightly below the boiling point of water at atmosphreric pressure to about 170°C at pressure equal to or greater than the vapor pressure of water at the temperature involved. The reaction mixture is subjected to mild agitation for periods ranging from about one day to several months to achieve the desired degree of crystallization to form the zeolite beta. Ewer temperatures will normally require longer periods in order to arrive at the desired crystal formation. For example, at temperatures of about 100°C crystal growth may occur during periods ranging from about one month to four months, whereas at temperatures near the upper end of the aforementioned range, e. g., about 160°C, the digestion period may be one or two days up to about one week. At intermediate temperatures of about 120° to 140°C, the digestion period may extend for about two to four weeks.

Any suitable templating agent may be used in forming the zeolite beta molecular sieve crystalline structure and, as indicated by the references referred to above, appropriate templating agents include tetraethylammonium hydroxides and halides such as tetraethylammonium chloride, dibenzyldimethylammonium hydroxide, or dibenzyldimethylammonium chloride. The reaction components may be varied in accordance with the techniques well known In the art to provide the zeolite beta product of varying silica/alumina ratios. Typically, the reaction mixture used to synthesize the zeolite beta molecular sieve will contain formulations within the following mole ratio ranges:

TABLE I

SiO_2/Al_2O_3:	20-1000
H_2O/SiO_2:	5-200
OH^-/SiO_2:	0.1-0.2
M/SiO_2:	0.01-1.0
R/SiO_2:	0.1-2.0

In Table I, R is the nitroorgano templating agent, e.g., a tetraethylammonium group and M is an alkali metal ion, usually but not necessarily, sodium. For a further description of zeolite beta and methods for its synthesis, recourse may be had to the above patents and patents applications including, specifically, U.S. Patent Nos. 3,308,069 (Wadlinger et al.) and 1,642,226 (Calvert et al.) the entire disclosures of which are incorporated herein by reference.

It is preferred that the initial beta zeolite has a silica to alumina ratio of between about 20 to 50. The as synthesized zeolite beta is initially subjected to an ion exchange step employing an ion exchange medium such as an aqueous solution of an inorganic ammonium salt, e.g., normal ammonium nitrate. Following the ion exchange treatment, the zeolite beta is subjected to calcination at a maximum temperature of about 570°C for a period of two or more hours. After the calcination treatment the zeolite beta is cooled and subjected to another ion exchange treatment which may be carried out with the same inorganic ammonium salt as described previously. At the conclusion of the second ion exchange treatment the zeolite beta normally will have a surface area at least twice that of the surface area of the original starting material and a very low sodium content. The sodium content, calculated as Na_2O, normally will be less than 0.04 wt.% and usually less than 0.02 wt.%. Following the second ion exchange treatment an additional, similar ion exchange treatment may also be employed. After drying, lanthanum is then incorporated into the zeolite system by ion-exchange method utilizing a lanthanum salt solution.

The lanthanum/beta zeolite is mixed with a binder such as alumina sol, gamma-alumina or other refractory oxides to produce a mulled lanthanum/beta zeolite-binder micture. The mixture is then pelletized by any suitable technique such as extrusion and the resulting pellets then dried, At this point, the pelletized binder-lanthanum/beta zeolite product is calcined under conditions sufficient to decompose the ammonium ions on the active site so the lanthanum/beta zeolite is placed in the active LaH-beta form.

In experimental work carried out respecting the present invention, a lanthanum/beta zeolite catalyst was employed in the reaction of ethylene and benzene to produce ethylbenzene. The parent zeolite beta catalyst was prepared by employing a multiple ion exchange and calcination procedure as described previously. The parent beta zeolite had a silica/alumina ratio of about 25, contained tetraethylammonium hydroxide as a retained templating agent, and had an initial surface area of 210 M^2/g and a sodium content of about 0.5-1% Na$_2$O. the initial ammonium ion exchange treatment was done by submersing the zeolite catalyst in an aqueous solution of ammonium nitrate having a normality of 2 at a zeolite to ammonium nitrate ratio of about 2:3. The zeolite beta was submersed in the ion exchange medium under mild agitation at 85°C for a period of two hours. The zeolite beta was then filtered and dried at 110°C for at least two hours. the dried powder was calcined at programmable temperature to a maximum of 570°C to burn the organic template. This calcined powder was thon ion-exchanged for two successive ion exchange with ammonium ions in a similar manner as described above. The surface area of the conclusion of the second ammonium exchange step was 750m^2/g. The sodium content was less than .01 wt.% Na$_2$.

Lanthanum was incorporated into the zeolite system by ion exchange method. Eighty (80) grams of anhydrous NH$_4$/Beta zeolite was suspended in deionized water. A salt solution of lanthanum nitrate was prepared by dissolving 1.247 grams of Na(NO$_3$)$_3$ in deionized water. This salt solution was slowly added to the zeolite suspension at a temperature of about 90°C. The exchange was continued for about 3 hours. This La-exchanged zeolite was filtered, washed and dried at 110°C. The chemical analysis of this powder form (La/NH$_4$beta-zeolite) is given below and shows a La content of about 0.1 wt.%.

Chemical analysis (anhydrous basis) of La/beta zeolite:

Sample	Wt%					SiO$_2$/Al$_2$O$_3$
	Si	Al	La	Na*	K*	
La/NH$_4$beta	43.2	2.7	0.12	0	0	30.9

*<0.01%

The powder lanthanum/beta zeolite (66.7 g, anhydrous basis) was mulled with nitric acid treated alumina (21.9 g, anhydrous basis) and extruded into 1/16 inch pellets. The resulting extruded zeolite pallets were then calcined in an oven under air in a programmed temperature to a maximum of 530°C. The LA/NH$_4$ beta catalyst was thus converted into La^{3+}/H-beta (La^{3+}=La$_2$O$_3$) catalyst as the NH$_3$ was evolved [$NH_4{}^+ \rightarrow NH_3 + H^+$] during calcination of the extrudates at 530°C. The final catalyst had following physical properties:

Surface Area=609.1 m^2/g
Micropore Area=325.0 m^2/g
Pore Volume=0.13 ml/g
Average Pore Diameter=33.1 A

The experimental work utilizing the lanthanum/beta zeolite was carried out in an upflow reactor heated by a sandbath set at a nominal temperature of 200°C. The reactor contained 9.06 grams of catalyst. The benzene was supplied to the bottom of the reactor at a rate to provide a space velocity (LHSV) of 12.2 hours to the -1 supplied to provide a benzene/ethylene mole ratio of 9.5, with the actual mole ratio varying during the experimental work from about 9.4 to 9.6, for comparative purposes, H-beta zeolite containing no lanthanum was utilized under identical alkylating conditions as the lanthanum/beta catalyst. The results of the foregoing experimental work are set forth below in Table II, and presented graphically in Figure 1. The effluent analysis is set forth in weight percent for benzene and ethylbenzene, and for various other components. The total xylene yields throughout the run are also set forth in Table II and Figure 1.

Table II

TIME, HRS H-BETA	PPM XYLENE RELATIVE TO ETHYLBENZENE	TIME, HR LA-BETA	PPM XYLENE RELATIVE TO ETHYLBENZENE
1.00	192.74	0.5	85.21
1.90	221.09	1.0	62.90
2.90	103.43	1.5	55.18
20.40	67.23	2.0	56.20
14.15	74.75	2.5	55.78
26.15	72.45	3.0	54.50
42.45	57.63	21.5	62.49
47.15	72.54	24.5	54.39
50.00	73.67	45.0	46.94
67.50	58.97	49.5	47.91
71.25	57.63	68.3	46.28
90.50	50.73	75.0	40.07
97.25	59.20	94.0	0.00
		99.0	0.00

Examination of the experimental data presented in Table II and bearing in mind that, for the most part, the ethylene charge to the reactor was slightly less than 12 percent of the stoichiometrically equivalent amount of benzene, it can be seen that the lanthanum beta zeolite catalyst is highly active and shows good selectivity to ethylbenzene production. The activity of the catalyst remained substantially undiminished after the duration of the experimental work.

In carrying out the invention, the alkylation reaction is carried out at a pressure well above the vapor pressure of the aromatic substrate at the reaction temperature involved in order to ensure that a liquid phase is retained in the reactor. An order to provide a complete liquid-phase reaction, a flooded bed format is used in which the catalyst bed is completely emerged in liquid. This can be readily accomplished using an upflow technique such as used in the experimental work and this usually will be preferred in carrying out the invention. However, downflow flooded bed operation can be accomplished by control of the outlet flow rate to ensure that the catalyst beds are covered by liquid benzene or other aromatic substrate.

Preferably a staged reaction format is employed in order to ensure good solubility of the ethylene (or other alkylating Agent) in the benzene (or other aromatic substrate) so that the entire reaction takes place in the liquid phase. In addition, use of multiple stages provides an opportunity for interstage cooling where adiabatic reactors are used or permits the use of several isothermal reaction stages. As noted above, such a staged reaction format is disclosed in copending application serial number 371,500. It is also preferred that the feedstocks be dehydrated prior to use in the present invention. A procedure for accomplishing such dehydration to provide a feed of reduced water content is described in copending application serial number 371,581, the entire disclosure of which is incorporated herein by reference.

Having described specific embodiments of the present invention, it will be understood that modification thereof may be suggested to those stilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

Claims

1. A molecular sieve catalyst comprising lanthanum/beta zeolite.

2. The molecular sieve catalyst as set forth in Claim 1, wherein the lanthanum content is between about 0.05

and 0.5 weight percent.

3. The molecular sieve catalyst as set forth In Claim 1, wherein the lanthanum content is about 0.1 weight percent.

4. The molecular sieve catalyst as set forth in Claim 1, wherein the surface area of said molecular sieve, based upon the crystalline structure of said lanthanum/beta zeolite is at least 650m²/g.

5. A molecular sieve catalyst as set forth in Claim 1, wherein said molecular sieve comprises lanthanum/beta zeolite in combination with a binder and wherein the surface area of said lanthanum/beta zeolite based upon the composite of said molecular sieve including said binder, is at least 450m²/g.

6. The molecular sieve catalyst as set forth in Claim 1, wherein said lanthanum/beta zeolite has a sodium content of less than 0.04 weight percent Na_2O.

7. The molecular sieve catalyst as set forth in claim 6, wherein said sodium content is less than 0.02 weight percent Na_2O.

8. In a process for the preparation of a lanthanum/beta zeolite derived by modification of an alkali metal containing zeolite beta synthesized by the hydrothermal digestion of a reaction mixture comprising silica, alumina, an alkali metal oxide, and an organic templating agent, the steps comprising:
   (a) treating said synthesized zeolite beta with an ion-exchange medium to proteinate a portion of the active sites in said zeolite by exchanging said alkali metal;
   (b) calcining under anhydrous conditions said ion-exchanged zeolite at a temperature within the range of 400°-700°C for a period within the range of 2-10 hours;
   (c) treating said calcining zeolite with an ion-exchange medium to proteinate an addition portion of the active sites in said zeolite by exchanging said alkali metal;
   (d) calcining under anhydrous conditions said ion-exchanged zeolite from step (c) at a temperature within the range an 400°-700°C for a period within the range of 2-10 hours;
   (e) incorporating lanthanum into said zeolite system by treating the ion-exchanged zeolite from step (d) with an ion-exchange medium comprising a lanthanum salt solution to obtain a lanthanum/beta zeolite;
   (f) fixing said lanthanum/beta zeolite with a binder to produce a mold lanthanum/beta zeolite binder mixture; and
   (g) pelletizing said lanthanum/beta zeolite binder mixture and drying the resulting pellets.

9. The method as set forth in Claim 8, further comprising the step of calcining said pellets at a temperature within the range of 520°-580°C for a period of 2-4 hours.

10. The method as recited in Claim 8, wherein the ion-exchange medium employed in step (a) is an aqueous solution of an ammonium salt.

11. The method as recited in Claim 8, wherein the ion-exchange medium employed in step (c) is an aqueous solution of an ammonium salt.

12. The method as recited in Claim 8, wherein the lanthanum salt solution employed in step (e) is an aqueous solution of lanthanum nitrate.

13. In a process for the liquid phase alkylation of aromatic compounds, the steps comprising:
   (a) supplying a feedstock containing an Aromatic substrate into a reaction zone and into contact with a lanthanum/beta alkylation catalyst;
   (b) supplying a C_2-C_4 alkylating agent to said reaction zone;
   (c) operating said reaction zone at temperature and pressure conditions to maintain said aromatic substrate in the liquid phase causing alkylation of said aromatic substrate by said alkylating agent in the presence of said catalyst; and
   (d) recovering alkylated aromatic substrate from said roaction zone.

14. The process as recited in Claim 13, wherein the surface area of said catalyst is at least 650m²/g.

15. The process as recited in Claim 13, wherein said alkylation catalyst comprises said lanthanum/beta ,zeolite in combination with a binder and wherein the surface area of said lanthanum/beta zeolite is at least

450m²/g based upon, said catalyst including said binder.

16. The process as recited in Claim 13, wherein said lanthanum/beta zeolite has a sodium content of less than 0.02 weight percent Na_2O.

17. The process as recited in Claim 13, wherein said lanthanum/beta zeolite has a sodium content of less than 0.02 weight percent Na_2O.

18. The process as recited in Claim 13, wherein the lanthanum content of said lanthanur/beta zeolite catalyst is between 0.05 and 0.5 weight percent.

19. The process as recited in Claim 13, wherein the lanthanum concern of said lanthanum/beta zeolite catalyst is about 0.01 weight percent.

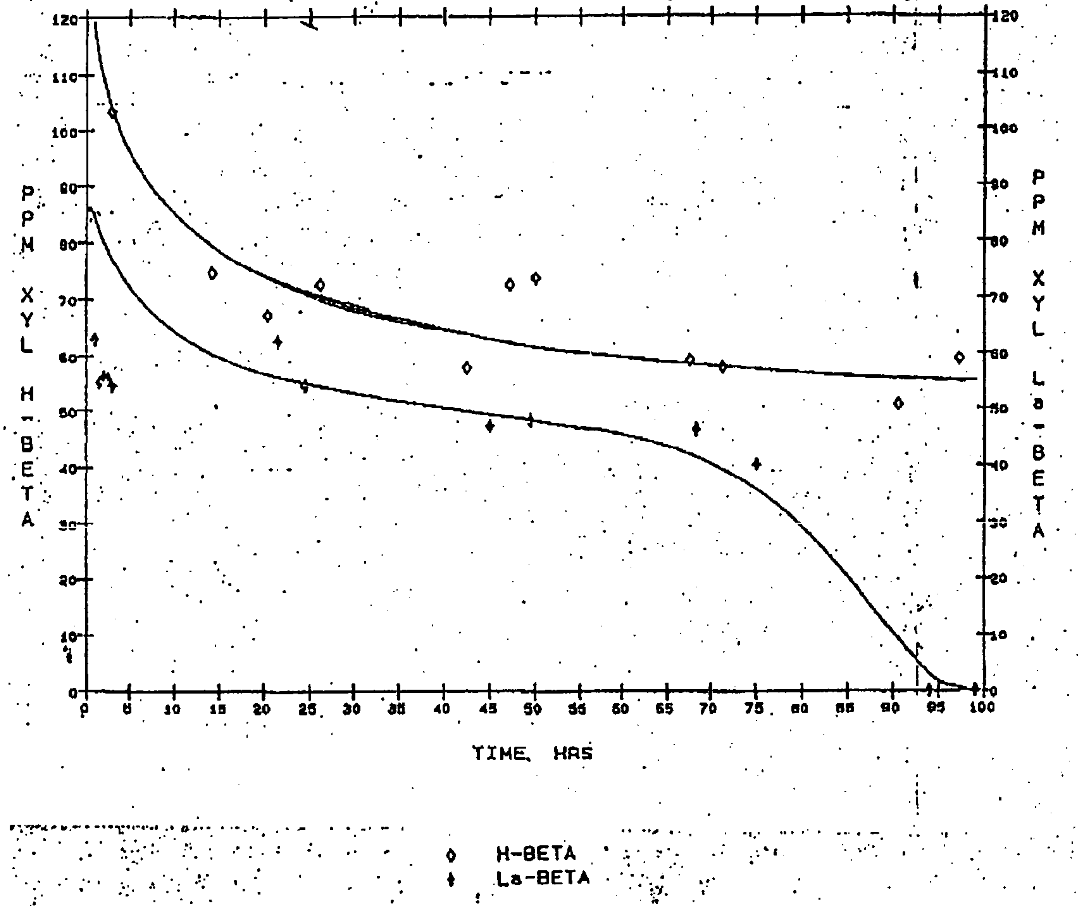
20. The process as recited in claim 13, wherein said aromatic substrate comprises benzene and said alkylating agent is an ethylating agent or a propylating agent.

21. The process as recited in Claim 20, wherein said alkylating agent is an olefin.

22. The process as recited in Claim 21, wherein said alkylating agent is ethylene.

Figure 1

XYLENES LEVELS FOR La AND H-BETA CATALYSTS. THE XYLENES ARE IN PPM AND ARE RELATIVE TO EB.



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 87 0056

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 338 734 (EXXON) * page 4, line 40 - line 45; claims 1-5 *	1-7	B01J29/28 C07C2/74
Y		8-12	
X	US-A-4 891 458 (INNES ET AL) * column 4, line 21 - line 40; claims 1-45 *	1-7, 13-22	
D,A	EP-A-0 159 846 (MOBIL OIL) * page 7, paragraph 2 - page 8, paragraph 2; claims 1-7 *	1-7	
Y	WORLD PATENTS INDEX LATEST Week 8743, Derwent Publications Ltd., London, GB; AN 87-305992 & SU-A-1 301 485 (AS BELO GEN INORG) * abstract *	8-12	
A	US-A-3 503 874 (UOP) * claims 1-16 *	8-12	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
			B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 JULY 1992	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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